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LEACHING OF SALTSTONE

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ABSTRACT

A modified IAEA leach test was used to evaluate the relative performance of potential saltstone formulations. The effects of sample size and leach rates for specific ions were determined. Leaching mechanisms were determined for NO_3^- , NO_2^- , SO_4^{2-} , Na^+ , Ca^{2+} and Si.

NO_2^- , NO_3^- , Na^+ and SO_4^{2-} are listed in order of decreasing leach rates. These ions exhibited high initial leach rates which decreased rapidly with time. High initial rates were attributed to surface wash off and diffusion. Within 10 days leach rates stabilized and can be explained by diffusion. Effective diffusivities for nitrite, nitrate, sodium, and sulfate were calculated from the leaching data. They are 6.4×10^{-10} , 4.1×10^{-10} , 3.2×10^{-10} , and 0.9×10^{-10} cm^2/sec , respectively.

Negative leach rates were measured for Ca^{2+} and Si in some formulations. This was attributed to precipitation of CaCO_3 and hydrated calcium silicate phases on the surfaces of the samples.

INTRODUCTION

Saltstone was developed as a cementitious waste form for disposal of Savannah River Plant (SRP) low-level radioactive waste [1]. Saturated leach tests are used as a criterion to evaluate the performance of candidate formulations. This study was also designed to identify leaching mechanisms and to evaluate the effects of sample size and sample surface area to volume ratios. Relative leach rates for various ions in saltstone were also determined. Results for two different formulations are presented here.

EXPERIMENTAL APPROACH

A modified IAEA leach test was used as a saturated analogue to unsaturated leaching in soil. In this test, leachate is periodically changed. In the unsaturated soil, percolating water in contact with saltstone monoliths will be continually replenished. The leachant used in this study was a natural spring water representative of Eastern coastal plain groundwaters. A typical composition is shown in Table I.

Leachate was changed every day for four days, once a week for the next four weeks, and every month thereafter. A low leachant volume to waste form surface area was selected to reflect, as closely as practical, unsaturated conditions. Volume of leachate was determined by multiplying the surface area by 2 cm and was held constant in order to evaluate rates without introducing other variables.

Final leachate analyses shown in Table I were corrected by subtracting the initial leaching solution composition from the final leachate composition. A typical leachate analysis is also shown in Table I. Leachates were analyzed for Ca^{2+} , Na^+ , and Si by plasma emission spectroscopy and for NO_3^- , NO_2^- , and SO_4^{2-} by ion chromatography. Duplicate samples were tested; actual values were typically within $\pm 20\%$ of the average. Leach rates were calculated according to Barnes, et al., 1982 [2].

TABLE I

Typical Leachant and Leachate Composition

	Thompson Spring Water 4/4/84 (mg/L)	Leachate Saltstone 84-40 14th Day (mg/L)	Representative SRP Groundwater (mg/L)
Na	19	245	3
Ca	51	1.66	2
Si	2.58	0.6/	1
NO ₃ ⁻	14.2	250	1
NO ₂ ⁻	0.08	69	<0.001
SO ₄ ⁻	25	36	1
pH	7.71	10.62	5.5

The influence of sample size and sample surface area to volume ratios were investigated using right cylindrical samples 2.5, 7.5, and 10 cm in diameter and height. Mix 84-40, the current SRP formulation was used in this evaluation. The composition of mix 84-40 is shown in Table II.

TABLE II

Composition of Formulations

Ingredient	PSU Mix Number	
	84-40 (wt%)	84-41 (wt%)
Class H Cement	12	12
Fly Ash (type)	48 (C)	38 (F)
Water	27.5	34
Salt	12.5	16
W/C	2.3	2.8
W/C effective*	0.45	2.8

* Class C fly ash is reactive and is considered cementitious. Class F flyash is not cementitious.

Mix 84-40 was also used to evaluate the relative leach rates of the various anions and cations in the waste solution. Cylinders 10 cm in diameter and height were used. Nitrite, nitrate, sulfate, and sodium were determined in the leachate.

Leaching characteristics of several formulations were also evaluated. Two formulations, mixes 84-40 and 84-41, are reported here for comparison. Cylinders 10 cm in diameter and height were used in the study. Physical properties of these mixtures are reported elsewhere [3].

Samples were prepared in a Hobart mixer with a whip attachment. They were cured for 28 days at 38°C and 100% RH prior to leaching. All samples were lightly sanded with 400 and 600 grit silicon carbide paper prior to leaching to ensure surface uniformity.

RESULTS

Effects of Sample Size and Surface Area/Volume

Differential leach rates (leach rate vs. time) and cumulative leach rates for nitrate are plotted in Figures 1 and 2, respectively, for 2.5, 7.5, and 10 cm samples of mix 84-40. For all three sample sizes, initial leach

rates (1-10 days) decrease more rapidly than they do between 10 and 100 days. This is shown by the steeper initial negative slopes for curves defined by these data. Since the data for the samples of various sizes follow similar trends, leaching mechanisms are assumed to be independent of sample size and sample surface area/volume.

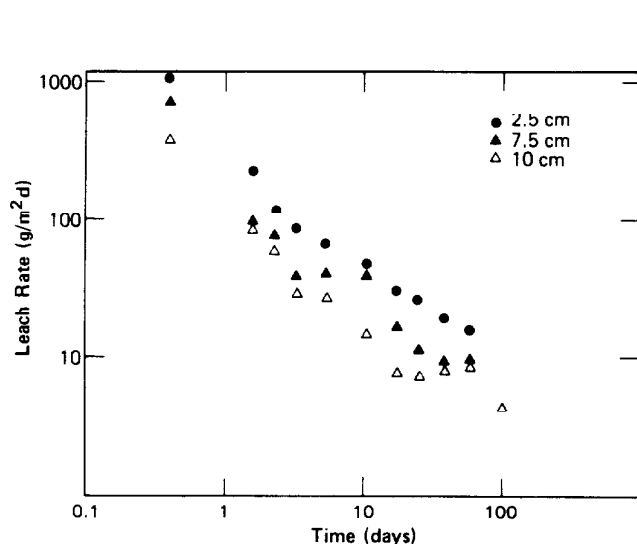


Figure 1. Log Nitrate Leach Rate Versus Log Time for Various Sized Samples of Mixture 84-40 (Each point is the average of two samples)

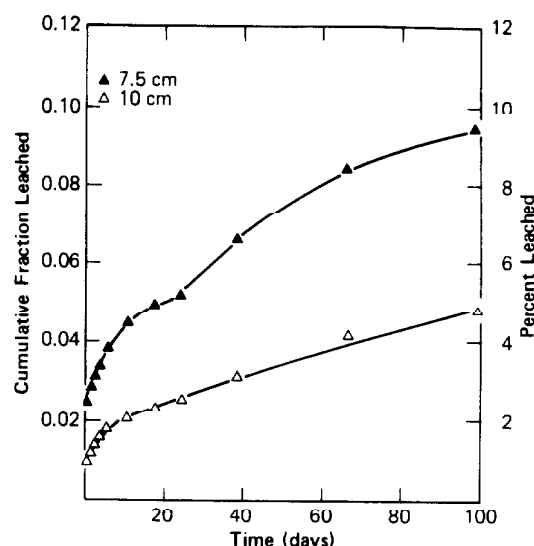


Figure 2. Cumulative Fraction Nitrate Leached Versus Time for 7.5 and 10 cm Samples of Mixture 84-40 (Each point is the average of two samples)

However, both sample size and surface area/volume ratios affect the total amount and cumulative fraction of nitrate leached. This is illustrated in Figure 2 for the 7.5 and 10 cm samples. The cumulative fraction leached from the 7.5 cm sample is about twice that leached from the 10 cm sample at any time up to 100 days.

A well defined zone 3-4 mm thick was visible on freshly fractured surfaces of leached samples (Figure 3). Leaching was normal to this zone. The thickness of this region is independent of sample diameter. In the 7.5 and 10 cm samples it accounts for about 16 and 10% of the total sample volume, respectively. This zone was interpreted to be the region of active leaching since the nitrate present in this volume alone can account for the cumulative amount leached through 100 days (about 4.7 and 9.3% of the total, respectively).



Figure 3. Macroscopic Zoning of Leached Saltstone Specimens

Leaching of Various Ions

Differential leach rates for various ions present in the initial waste solution are plotted in Figure 4. NO_2^- , NO_3^- , Na^+ , and SO_4^{2-} are listed in order of decreasing leach rates. Differences in leach rates for these ions are relatively small. Therefore, they are best illustrated in plots of cumulative fraction leached versus time, where differences are summed over time, Figure 5.

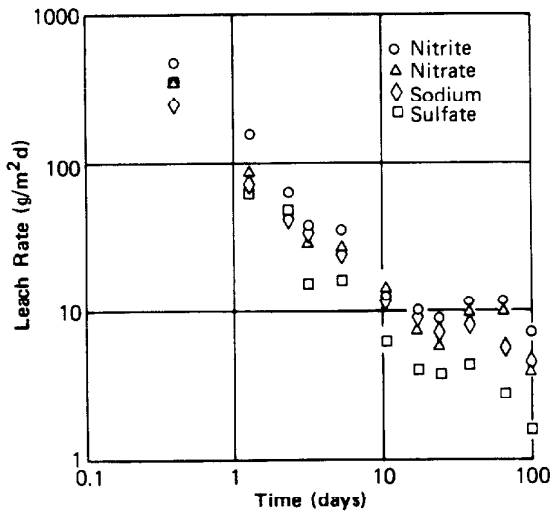


Figure 4. Comparison of Leach Rates for Nitrite, Nitrate, Sodium and Sulfate in 84-40, 10 cm Samples (Each point is the average of two samples)

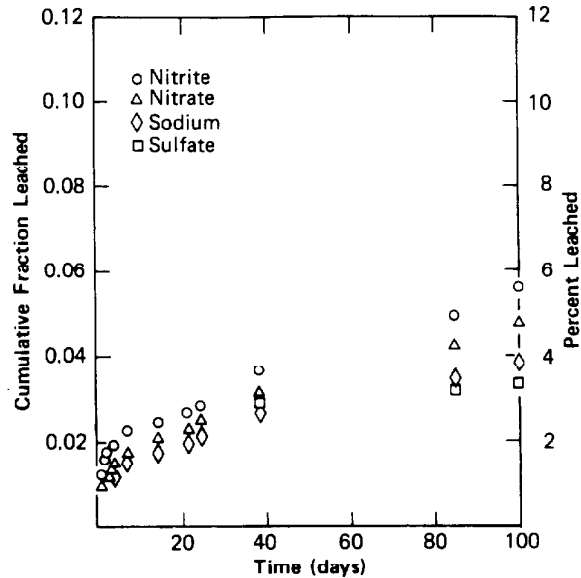


Figure 5. Cumulative Fraction Leached Versus Time for Mixture 84-40 (Each point is the average of two samples)

The time dependency of leach rate is similar for these ions. It is characterized by an initial rapid decrease in rate between 1 and 10 days. At later times, the decrease in leach rate is slower.

Leach rates for elements which form the matrix of the cement-based waste form were also measured. This material consists of x-ray amorphous hydrated calcium silicates and aluminates. Calcium in particular had a negative leach rate. Calcium present in the initial leachant was removed from solution and deposited on the surface of the waste form as CaCO_3 . The rate at which calcium was removed from the leachant was dependent on the concentration in solution, volume of solution, and number of changes of leachate. A surface layer of calcite and aragonite on a leached specimen of mix 84-40 is shown in Figure 6.

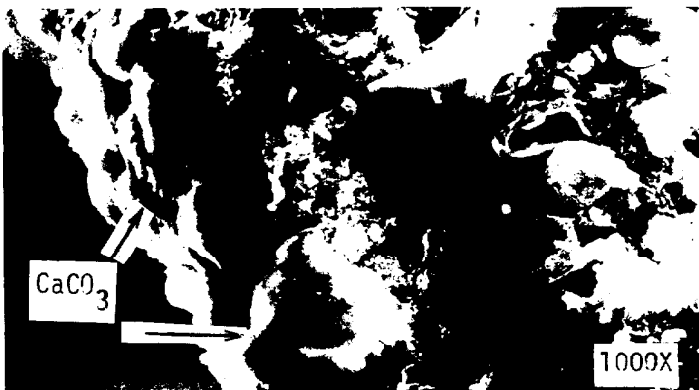


Figure 6.
 CaCO_3 Deposited on the Surface of Leached Sample (84-40)

Silicon has a low constant leach rate of less than 5×10^{-4} g/cm²-day for mix 84-40. In some low silica formulations such as mix 84-41, silicon also has a negative leach rate. In this mix, the concentration in solution decreased with time. This suggests that a calcium silicate phase is precipitated on the leached surface of mix 84-41.

Comparison of Different Formulations

Nitrate leach rates vs. time are plotted in Figure 7 for mixes 84-40 and 84-41. Mix 84-40, the current SRP reference formulation, is characterized by a lower leach rate. This mix also has a lower porosity, 38% compared to 60%, and a lower water permeability, 10^{-11} cm/sec compared to 10^{-6} cm/sec for mix 84-41 [3].

The differential nitrate leach rates for these two mixtures show a strong time dependency. Initially, the slopes of these curves are steeper than at later times (after 10 days). However, additional data are required to evaluate the mechanisms controlling long-term leaching.

Cumulative nitrate leach rates for mixes 84-40 and 84-41 are plotted in Figure 8. After 10 days, about 2% of the total amount of nitrate was leached from mix 84-40 whereas about 5% was leached from mix 84-41. After 50 days, about 3.5% of the nitrate was leached from mix 84-40 compared to 9.1% from mix 84-41.

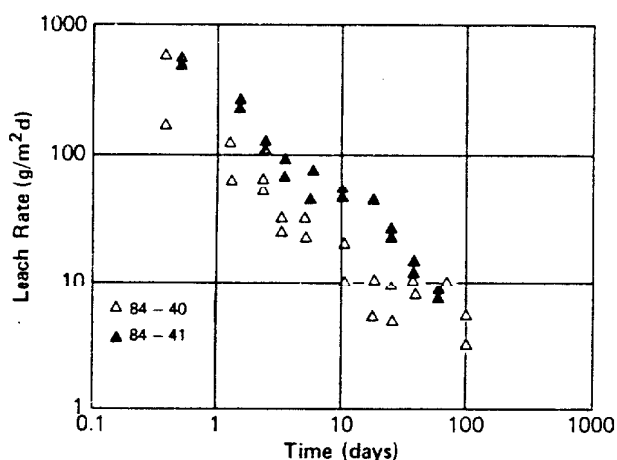


Figure 7. Log Nitrate Leach Rate Versus Log Time for Mixtures 84-40 and 84-41. Data from Duplicate Samples are Plotted.

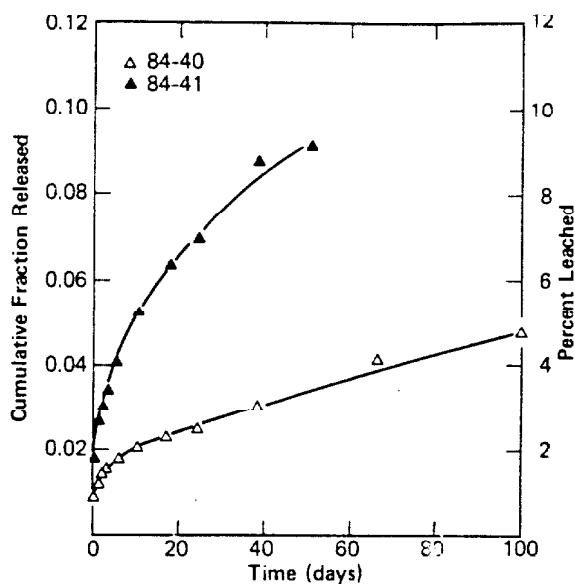


Figure 8. Comparison of 84-40 and 84-41: Cumulative Fraction of Nitrate Leached Versus Time (Each point is the average of two samples)

Sodium and sulfate differential leach rates are also plotted for mixes 84-40 and 84-41 in Figures 9 and 10, respectively. A break in slope of these differential leach rate curves occurs between 1 and 3 days for mix 84-41. It occurs between 5 and 10 days for mix 84-40. Initially, the time dependency of leaching is greater than at later times. Leach rates for sodium and sulfate in mix 84-41 are approximately equal. However, in mix 84-40, sulfate leaches more slowly than sodium after about 10 days of testing.

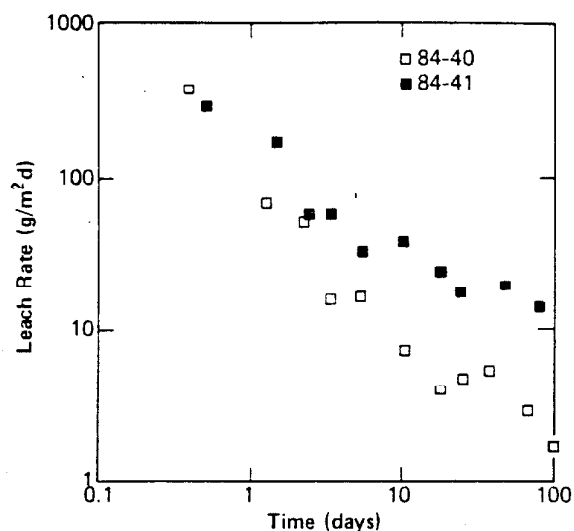


Figure 9. Log Sodium Leach Rate Versus Log Time for Mixtures 84-40 and 84-41 (Each point is the average of two samples)

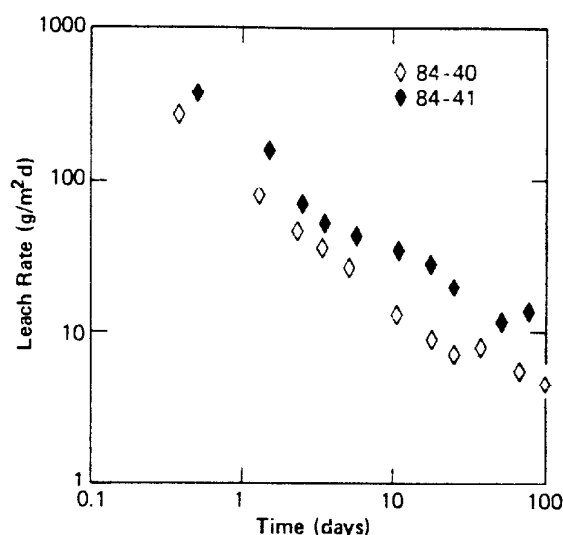


Figure 10. Log Sulfate Leach Rate Versus Log Time for Mixtures 84-40 and 84-41 (Each point in the average two samples.)

DISCUSSION

Leaching data were examined to determine whether diffusion can account for the rates calculated in this study. In cases where leach rates could be explained by diffusion, diffusivities were calculated for relative comparisons according to equation (1) [2,4].

$$D = \frac{\pi}{4} \left\{ \frac{d((A_i/A_0)/(V_{\text{solid}}/S))}{d(t^{1/2})} \right\}^2 \quad (1)$$

where

- A_i = amount of species i leached
- A_0 = amount of species i in sample at start
- V_{solid} = volume of solid sample (cm^3)
- S = surface area of sample (cm^2)
- t = time in seconds

This relationship can be rewritten as $\frac{\delta C}{\delta t} \propto t^{-1/2}$ or as $\log(\text{rate})/\log(\text{time}) \sim -1/2$ [2].

Diffusivities, calculated from equation (1), are called effective, $D_{\text{effective}}$, because there is a fundamental problem in the choice of S , the surface area of the solid being leached. Macroscopic surface areas calculated from exterior dimensions were used in these calculations.

Leaching Mechanisms

In this study, differential leach rates were plotted as log rate vs. log time. In general, the averaged data plot as curves with a slope of $-1/2$ for times between 10 and 100 days. This was interpreted as evidence that the mobilities of NO_3^- , NO_2^- , SO_4^{2-} , and Na^+ in the leaching systems studied are controlled by diffusion after an initial period (up to 10 days).

Initial leach rates were consistently high and were characterized by greater time dependencies than those measured at later times. This was attributed to a combination of mechanisms such as diffusion plus surface wash off contributing to ion mobility. A decreasing influence of surface wash off with time and possibly blockage of some surface pores with CaCO_3 or cement hydration products may be responsible for the greater negative time dependence (higher negative slope) during the initial leaching period.

The transition period between high initial leach rates and later diffusion-controlled rates corresponds to the transition between changing leachate every day and changing it once a week. Therefore, to some extent, the initially high rates may have been exaggerated by the test method.

Relative Ion Diffusivities

Plots of $(\Sigma A_i/A_0)(V_{\text{solid}}/S)$ versus $t^{1/2}$ were constructed for the four ions whose mobilities can be accounted for by diffusion between 10 and 100 days of leaching. These plots are shown in Figure 11 and can be approximated by straight lines with positive slopes. This would be expected for diffusion-controlled leach rates. Offset in the positive direction reflects high initial leach rates which were attributed to a combination of diffusion and other processes such as washoff.

Plots shown in Figure 11 follow a similar trend with the exception of SO_4^{2-} . This can be explained if the sulfate source term is adjusted to account for the SO_4^{2-} in the cement as well as that in the solution. This will result in a larger A_0 term and consequently smaller (cumulative fraction leached)(V_{solid}/S) values. The reaction of some SO_4^{2-} to form hydrated calcium aluminate sulfate phases in the cement matrix can also account for the lower slopes.

The slope for the nitrite plot is slightly steeper than those for nitrate and sodium. Since there are no known nitrite compounds in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system and since nitrite is not present in the cement or starting leachate, the A_0 term for NO_2^- is unaffected by cement hydration reactions. However, small amounts of nitrate can be incorporated in the structures of some hydrated calcium aluminate sulfate phases. Sodium substituted hydrated calcium silicate phases were detected in these waste forms [3]. Removal of small amounts of these constituents from the pore solution may account for these differences in slopes in Figure 11.

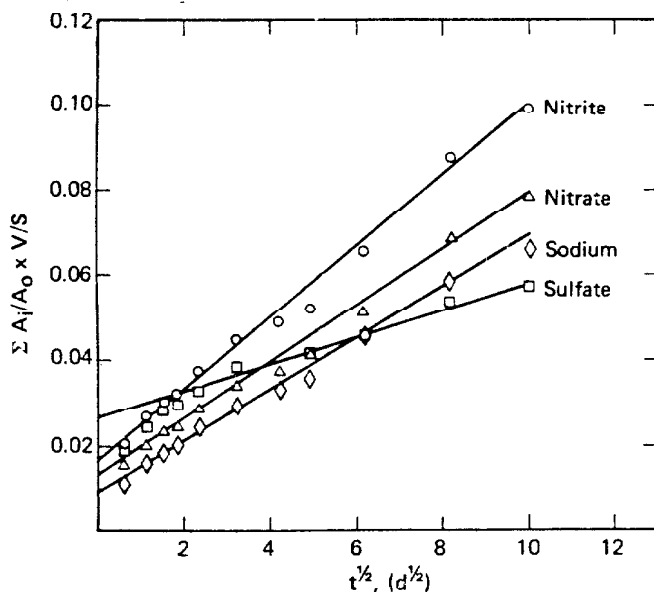


Figure 11. Cumulative Amount Leached (Normalized) Versus Time^{1/2}

Values for effective diffusivities were obtained from the slopes of the curves in Figure 11, $D_{\text{eff}} = \frac{\pi}{4} (\text{slope})^2$. Values for NO_2^- , NO_3^- , SO_4^{2-} , and Na^+ are within the same order of magnitude, 10^{-10} cm^2/sec , and are given in Table III.

TABLE III

Effective Diffusivities for Ions in Mixture 84-40
Calculated from Leaching Data (10 cm samples)

<u>Ion</u>	<u>$D_{\text{effective}}$ (cm^2/sec)</u>
NO_2^-	6.4×10^{-10}
NO_3^-	4.1×10^{-10}
Na^+	3.2×10^{-10}
SO_4^{2-}	0.9×10^{-10}

Effects of Sample Size

Effective nitrate diffusivities can also be used to compare ion migration from samples of different sizes. For the 7.5 cm sample, the effective nitrate diffusivity is 9.1×10^{-10} cm^2/sec . This is higher than the value calculated for the 10 cm sample, 4.1×10^{-10} cm^2/sec . This difference may indicate several things including: the assumptions made in solving the diffusion equations do not completely apply to the system studied, and/or the effective surface area is important and is a function of sample size and geometry.

Variation Among Formulations

For comparison between formulations, the effective nitrate diffusivity was also calculated for the 10 cm sample of mix 84-41. It is 2.3×10^{-9} cm^2/sec compared to 4.1×10^{-10} cm^2/sec for mix 84-40. Higher effective diffusivities in mix 84-41 can be related to a higher porosity and greater fraction of large pores for mix 84-41 compared to mix 84-40.

CONCLUSIONS

Nitrite, nitrate, sodium, and sulfate are listed in order of decreasing leach rates and effective diffusivities for saturated leaching of saltstone. High initial rates were attributed to surface wash off and diffusion. Blocked surface pores caused by cement hydration products or calcite formation may also account for the high negative time dependencies initially measured. Stabilized leach rates for all the ions and waste forms tested can be explained by diffusion.

Effective diffusivity data for NO_2^- , NO_3^- , SO_4^{2-} , and Na^+ can also be used to support the existence and importance of an interfacial region. Diffusivities measured in the bulk material are about 10^{-7} cm^2/sec [3]. Effective diffusivities calculated from leaching data range from 10^{-9} to 10^{-10} cm^2/sec . These lower effective values may depend on concentration gradients and pore properties in this interfacial region. This situation is also expected when saltstone is in contact with unsaturated soil. Therefore field tests and unsaturated soil column tests are being conducted to evaluate in-migration rates under disposal environment conditions.

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